THE EISENHOWER LIBRARY
3 1151 02691 9252

Library
THE JOHNS HOPKINS UNIVERSITY BALTIMORE 1876
VERITAS VOS LIBERABIT
of the
Johns Hopkins University

A STUDY OF THE VAPOR PRESSURE AND OSMOTIC PRESSURE OF AQUEOUS SOLUTIONS OF MANNITE AT TWENTY DEGREES.

BY

THOMAS HUNTON ROGERS.

DISSERTATION

Submitted to the
Board of University Studies of the Johns Hopkins University
in conformity with the requirments for the
Degree of Doctor of Philosophy.
Baltimore 1917.

CONTENTS

ACKNOWLEDGEMENT

INTRODUCTION 1

EXPERIMENTAL

Series I 3

Observations 5

Data 7

Series II 9

Preparation of Solutions 9

Observations 11

Analysis of Solutions 13

Data 15

DISCUSSION OF RESULTS

Accuracy of Method 27

Raoult's Law 28

Von Babo's Law and Heat of Dilution 31

OSMOTIC PRESSURE

Experimental 36

Data 38

Osmotic Pressure and Vapor Pressure 38

SUMMARY 41

BIOGRAPHY

ACKNOWLEDGEMENT

This investigation was carried out under the direction of Professors Frazer and Lovelace, to whom the author wishes to express his sincere appreciation of the inspiration and assistance they gave.

He also wishes to acknowledge a debt of gratitude to them as well as to Professors Morse, Remsen, Reid, the late Professor Jones, and to Doctors Shenton and Bateman for instruction in the lecture room and laboratory.

THE VAPOR PRESSURE LOWERING AND OSMOTIC PRESSURE OF MANNITE SOLUTIONS.

INTRODUCTION

The superiority of the vapor pressure method of investigating the colligative properties of solutions is largely recognized. In addition to the fact that any temperature is available, which is not the case in cryoscopic work, the value of the vapor pressure of a solution, once determined, is affected by hardly any conditioning factors. the fundamental importance of a knowledge of the vapor pressure of solutions is illustrated by the frequent occurence of such a term in thermodydynamic formulae. This is because the vapor pressure of a perfect solution is a measure of what has been called its escaping tendency.

In 1913 Frazer and Lovelace devised an improved static method[1] for measuring the lowering of the vapor pressure of solutions, in which they overcame the principal difficulties encountered by previous investigators. The static method was chosen because the correctness of results obtained by the dynamic methods is not unquestioned. Further many possibilities of error were eliminated by making the method a differential

[1] J.Am. Chem. Soc. 36, 2439 (1914); Z. Phys.Chem.,89,155.

one, comparing directly the pressures above solution and pure solvent which were contained in an accurately regulated temperature bath. Accuracy of measurments was obtained by the use of the Rayleigh manometer.

After some preliminary work on mannite solutions the meth- was improved in 1914 by effecting a more delicate temperature regulation and an efficient means of stirring the solutions and solvent, and the lowering of five concentrations of mannite was determined.[1] In the course of the work certain slight sources of error were recognized and, after eliminating these, the investigation was ex tended to potassium chloride solutions[2].

Accordingly it has seemed desirable to repeat the work on mannite under the most favorable conditions, inasmuch as it is important to determine carefully the lowering of a representative non-electrolyte, and , of the common compounds, mannite seems to behave as nearly normal as any other. It also seemed desirable to determine the osmotic pressure of these solutions at the same temperature and thus investigate the quantitative relation between these properties.

EXPERIMENTAL

Series I The apparatus used was that described in the work on KCl solutions[2]. A sample of mannite which had been purified in the course of the investigations on osmotic pressure in this laboratory was used thruout.

[1]R. N. Mullikan, Dissertation, Johns Hopkins Univ. 1915.

[2]Frazer, Lovelace and Miller, J.AM··Chem. Soc.,38,516,(1916).

The experimental details were carried out in this series in practically the same manner as in the previous work. The solutions were subjected to a preliminary removal of air by repeatedly exhausting the space above the solution contained in a specially constructed flask. This was done by taking advantage of the expansion of the solution on raising the temperature when the flask, completely filled with solution, was sealed shut at the cappilary opening. The solutions were further freed from air after they were introduced into the bath. Often the vapor was allowed to expand into an evacuated bulb as many as twenty five times before the solution was sufficiently air-free to take observations. The test for air was made by measuring with the McLeod gauge the residual pressure after the liter bulb, which contained the vapor from a solution, had been opened to the phosphorous pentoxide.

To ensure equilibrium between liquid and vapor phase before testing, the solution was left open to the bulb for twenty four hours with intermittent stirring. When now the test was made, it was observed that while practically allthe vapor seemed to be absorbed in perhaps a half hour, still a further slow absorption took place for a number of hours. At the end of about twelve hours the reading on the gauge became constant and, if the pressure indicated was 0.0005 mm. or less, the test wasconsidered satisfactory and the air present deemed negli-

gible. While this behavior occasioned surprise, especially the slowness of the absorption, its significance was entirely overlooked during this series.

Observations.

Acareful study of the proper conditions for taking observations was made. Inthe light of the previous work it was obvious that an essential condition is that the temperature of the room should be fairly constant. At first a small electric fan was used in an attempt to prevent conduction of heat from the observer's body to the system. It was thought that this might also aid in keeping the room at somewhat the same temperature. However the readings under these conditions were erratic and frequently a sudden change in pressure could be seen in the manometer, even tho the bath temperature was perfectly constant. This led to an attempt to regulate the temperature of the room. But, tho it was found that a constant reading could,under the most favorable conditions of regulation, be obtained, in generalthe effect was much worse for the system containing the vapor was subjected to very slight but sudden changes of temperature, as a rapid motion of the air was necessary for effecting regulation. This effect was that equilibrium between liquid and vapor phase was constantly disturbed. Hence the solution of the difficulty came in exactly the opposite direction

If the room temperature be kept reasonably constant and there is no stirring of the air the effects of diffusion are

sufficiently slow so that condensation or evaporation will take place at the surface of the solution, constantly equilibrating the vapor pressure. When all openings to the room are closed tight and the source of heat kept constant, a few minutes thereafter readings can be taken.

After removal from the bath the solutions were analyzed both by the use of the interferometer and by evaporating a weighed portion to dryness, heating the residue to constant weight at 130°. The results of the two methods accorded well.

Table I gives in brief the results of this (preliminary) investigation of the lowering of ten concentrations of mannite solutions. Column 1 gives the concentration expressed, mols (0.16) of solute per 1000 grams of solvent. Column 3 gives the lowering produced in millimeters of mercury. This value is uncorrected, being in terms of mercury at the prevailing room temperature.

For the sake of comparison column 2 gives the lowerings found by Mullikan[1], expressed similarly. His data have been extrapolated over a slight range in order to get values corresponding to the concentrations in column 1.

Column 4 shows the theoretical lowerings of these solutions as calculated from Raoult's law, and under the same conditions as the values in columns 2 and 3.

Column 5 gives the deviations from Raoult's law of the values found inthis series.

[1] Mullikan, Dissertation.

Table 1 -- Comparison of the Values Obtained for the Lowering of Mannite Solutions.

M	Mulli-kan	Series I	Calcu-lated	Differ-ence	Series II
0.0995	0.0287	0.0280	0.0314	0.0034	0.0311
0.1993	0.0587	0.0585	0.0627	0.0042	0.0620
0.2985	0.0906	0.0882	0.0939	0.0057	0.0930
0.3984	0.1188	0.1221	0.1251	0.0030	0.1239
0.4986	0.1538	0.1533	0.1563	0.0030	0.1553
0.5968		0.1819	0.1867	0.0048	0.1869
0.6960		0.2127	0.2175	0.0048	0.2173
0.7958		0.2471	0.2489	0.0018	0.2491
0.8944		0.2740	0.2784	0.0044	0.2802
0.9941		0.3061	0.3088	0.0027	0.3108

Column 6 gives the values found in series II (vide infra) extrapolated and expressed similiarly.

The agreement of the results in this series with those of Mullikan is fair, though in several cases there is greater deviation than the 0.001 mm claimed as the accuracy of the method. However, the nearly constant deviation from Raoult's law was suspicious, especially in the concentrations where agreement would most be expected. In order to make certain that the solutions measured were free of air another method of preliminary removal was devised. This will be described in series II where it was found that solutions so prepared gave a lowering from 0.003 — 0.004 mm higher than those recorded in series L. Further, when tests for air were made on the solutions of series II, the readings on the McLeod gauge showed negligible air pressure after twenty minutes absorption

by the phosphorous pentoxide. This difference in behavior was obviously due to the fact that the solutions of series I were measured with an air pressure of 0.003 — 0.005 mm. The gauge readings on air tests should have been made after the same length of time, twenty minutes, whereupon the air present would have been discovered. If the pentoxide is kept open for a longer time adsorption of the residual air takes place slowly, both by the pentoxide and the glass surfaces of the system. Since all solutions investigated in previous work had quite an amount of air in them, the agreement in some cases may seem surprising. But this is explained by the fact that the same techniques of preparation of solution was used throughout and the same criterion adopted for a test, the result being that very nearly the same amount of air was left in practically every case.

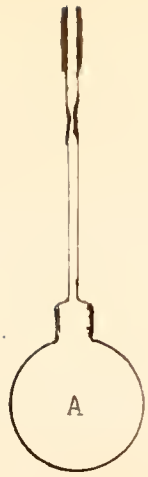

Figure 1

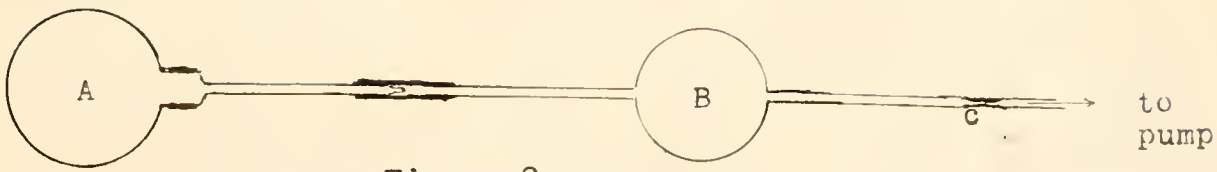

Figure 2

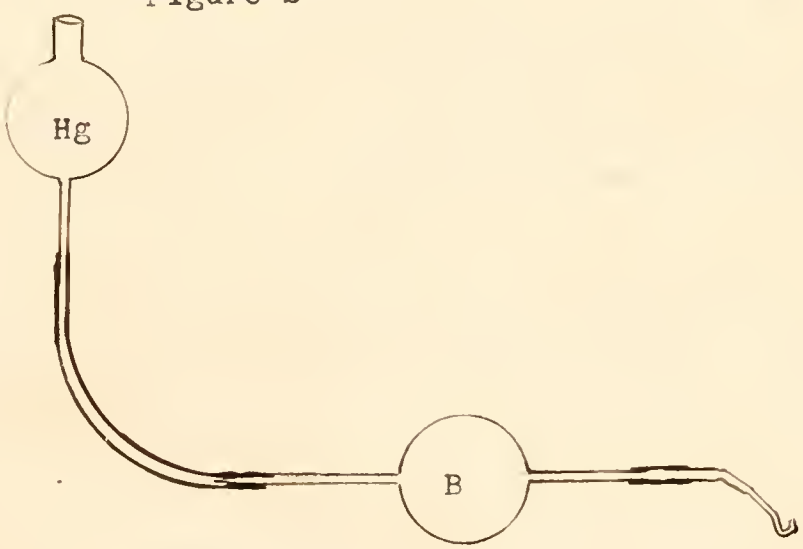

Figure 3

Apparatus employed in Making up and

Introducing Solutions.

Series II

Preparation of the Solutions. In order that the solutions might be made up to a definite concentration it seemed best to first free both solvent and solute of air and then mix the two. After several trials the following method was found to be simple, rapid and efficient.

The water is introduced into a 500 cc flask to which is sealed a length of 7 mm glass tubing (A, figure 1). Near the end of the tube a constriction is drawn and a short piece of tubing fitted on the end. After boiling the water vigorously for 35 minutes, the rubber tube is suddenly pinched shut, at the same time removing the flask from the source of heat. The tube is then sealed at the constriction. The flask has been previously weighed, and by weighing the sealed flask and tip the weight of the water is found.

An amount of solute corresponding to the weight of the water is introduced into the flask B (figure 2). After scratching the tip the tube of flask A is joined to B by means of a stout rubber tube. The other end of B is connected to the vacuum pump and, after several hours exhaustion, is sealed shut at the constriction c. The tip of A is then broken and the constituents mixed. In order to introduce the solution, the connecting rubber tube is pinched shut, the flask A removed, and a special pipette put in its place. The other end of flask B is connected to a mercury reservoir (figure 3), and the tip broken under the mercury in the rubber

tube. Under pressure from the reservoir the solution is forced through the pipette, the end of which is placed under the surface of the mercury at the bottom of the tubes which go into the constant temperature bath.[1] The solution now bubbles up through the mercury until the bulb in the bath is nearly full.

Solutions prepared and introduced in this manner require only a few vapor expansions in the bath in order to completely remove the air. The use of rubber tubing for a connection in the apparatus (figure 2) cannot be conveniently avoided and no trouble from leakage was experienced after a good grade of antimony rubber tubing was selected and care was taken to wire the ends. Absolutely complete removal of air in the preparation of a solution was not attempted, as there is always some air taken up in introducing, due to the slight amount of air in the mercury and a certain amount trapped by the mercury column on the walls of the tubes leading up into the bath. The flask in which the water was boiled was steamed out thoroughly before using. After this a sample of water which had been boiled in the flask for thirty five minutes was compared in the interferometer with a sample of conductivity water. The difference in density was found to be very slight and certainly not enough impurities were present to effect a lowering of the vapor pressure. In this work either conductivity water or recently distilled water, which compared favorably in the interferometer with conductivity water, was used throughout.

---

1. See figure 1, J. Am. Chem. Soc., 38, 517 (1916)

Observations. The readings were taken under conditions as described in series I. Frequently observations were attempted before the solutions were air free, as in this way the rate of the removal of air could be follwed. Hence these preliminary readings were not reliable and no results are recorded here until the solutions had been shown to have less than 0.0004 mm. The exact reading of the McLeod gauge is a little unsatisfactory at this slight pressure, but it is safe to say that the maximum air pressure of a solution considered air free was this amount, while frequently it was much less. At the time of making readings the residual air was certainly less for the solution and solvent were subjected to a fresh vapor expansion just before observations were made.

Constant readings can be taken within fifteen minutes after opening a solution to an evacuated bulb. If appreciable air were present in the solution the deflection would not be constant, due to air coming out of the solution. This phenomenon was actually observed in many preleminary observations on solutions known to contain air, when the readings would gradually drop. When the solution is once freed of air no trouble is experienced in getting a series of concordant measurements.

The observations were continued until at least five consecutive concordant sets were obtained. In these final measurements as recorded here no values have been thrown out unless the data was unreliable for obvious reasons, such as the loss

of the zero point, or a change in bath temperature. A few non-concordant values are bracketed . Some readings were taken while the solutions were being stirred at a variable speed by means of an arrangement constructed by Mr. Sease. The deflections were found to be independent of the rate of stirring, so that practically all of the observations were made with constant speed stirring. The arrangement mentioned was such that the rate of stirring was changed over a wide range several times each minute, thus effectually preventing surface concentration.

The zero point of the measurement is given by the setting of the manometer when the limbs of this instrument are open to one another. This reading was always taken before and after each reading of the deflection of the solution. Sometimes, due to slight unsteadiness of the mountings of the telescope, the zero value was not checked. In such cases the reading of the deflection was taken again. If the two values checked, these two deflections, together with the included zero point, were used to compute the lowering.

During a large part of the work a paper scale was used to measure the deflections. This scale was inaccurate, but it was carefully calibrated over exactly the range which was used to measure the deflection, at the time when the scale was used for that particular deflection. As soon as the readings were obtained on a given solution the scale was removed and compared with a standard meter by means of a cathetometer. The deflec-

tions of the solutions investigated after December 1 1916 were measured by a silver scale which was found to be correct.

To calculate the lowering, the scale deflection, s, the distance between the points of the manometer, d, and the distance from the mirror on the manometer to the scale, D, must be known. The lowering, h, is given by the expression[1]

$$h = \frac{d}{2D} s \quad \text{or,} \quad h = ks.$$

This involves the assumption that $\sin \theta = \frac{1}{2} \tan 2\theta$, where θ is the angle of tilt of the manometer. This assumption is found not to introduce an appreciable error in the case of the most concentrated solutions investigated. The value of d for the manometer was redetermined and the length, D, was frequently checked off. The values of h thus calculated is the height of a column of mercury at room temperature, about 24°. This is corrected to the height of a column of mercury at zero degrees, which is the lowering $p_o - p_1$.

Analysis. After taking due precaution to keep the solution as near as possible to the original concentration in removing it from the bath, the exact concentration was determined. The Rayleigh-Zeiss interferometer served admirably for this purpose. With a twenty millimeter cell a solution can be compared with a standard with as great an accuracy as that with which the standard can be compared. By making a rough analysis and then preparing a standard very nearly the concentration of

1. J. Am. Chem. Soc. 36, 2440 (1914)

the solution being analyzed the interferometer serves practically as a zero instrument. Often as a check the weighed portion of a solution was evaporated to dryness and the residue dried to a constant weight at 130. These results accorded well with those from the interferometer method. No trouble was experienced in getting a constant weight of the mannite residue, an objection mentioned by Flügel[1]. The molarity was thus easily determined with an accuracy of 2×10^{-4} weight molar, which corresponds to a vapor pressure lowering of less than 0.0001 mm. The concentration was always expressed in terms of mols of mannite per 1000 grams of water, the weights being reduced to the vacuum standard, and 182.12 employed as the molecular weight of mannite.

A tabulation of the results for 12 concentrations of mannite solutions follows.

1. Flugel, Z. physik. Ch., 79, 577 (1912)

0.09845 M Mannite

Date	Zero	Reading	Zero	Deflection
11/8/16	1.1	7.2		
	1.0	7.0		
	0.95	7.1	0.95	
	1.0		1.0	6.10
11/9/16	1.0	7.1		
	1.05	7.05	1.05	
		7.1	1.1	6.01
11/9/16	1.9			
	1.8	7.9	1.9	
	1.75	7.9	1.8	
	1.8	7.95	1.7	6.11
11/10/16	0.95	7.0		
	1.0	7.0	1.0	
		7.0	0.95	6.02
11/11/16	2.0	8.1		
	2.0	8.15		
		8.0	2.05	
		8.1	2.05	6.08
11/11/16	2.8	8.9		
	2.8	8.95	2.8	
	2.9	8.85	2.9	6.06
				———
		Average Deflection		6.06 mm

k = 0.005080

0.1977 M Mannite

Date	Zero	Reading	Zero	Deflection
10/27/16	3.6	15.7		
	3.6	15.85		
		15.8	3.6	12.18
10/28/16	2.0	14.0		
	1.95	14.0		
		14.05	2.0	12.04
10/29/16	1.0	13.15	1.0	
	1.05	13.2	1.05	
		13.1	1.0	12.13
10/30/16	3.0	15.1		
	3.0	15.15	2.95	
		15.05	3.0	12.11
11/1/16	2.9	15.0		
	2.8	14.95	3.0	
	2.85	15.0	3.0	12.13
11/1/16	2.1	14.15		
	2.05	14.1		
		14.2	2.05	
		14.2	2.05	12.10
11/4/16	3.05	15.1		
	3.05	15.1	2.95	
		15.05	3.0	12.07
				———
		Average Deflection		12.11
		Scale Corrected		12.15 mm

k = 0.005080

0.2962 M Mannite

Date	Zero	Reading	Zero	Deflection
11/8/16	1.1			
	1.0	19.15		
	0.95	19.2	0.95	
	1.0	19.15	1.0	18.17
11/9/16	1.9			
	1.8	20.0	1.9	
	1.75	19.95	1.8	
	1.8	19.95	1.7	18.16
11/10/16	0.95	19.2		
	1.0	19.2	1.0	
		19.2	0.95	18.22
11/11/16	1.95	20.2		
	2.0	20.1		
		20.05	2.0	
		20.2	2.0	18.15
11/11/16	2.8	21.1		
	2.8	21.05		
	2.9	21.0	2.8	
		21.0	2.9	18.20
			Average Deflection	18.18 mm
			Scale Corrected	18.23 mm

k = 0.005080

0.3949 M Mannite

Date	Zero	Reading	Zero	Deflection
11/18/16		26.7		
		26.65		
		26.65	2.5	
		26.6	2.5	24.15
11/18/16	2.1	26.35		
	2.1	26.2		
		26.25	2.1	24.17
11/19/16	1.15	25.25		
	1.05	25.3	1.05	
	1.1	25.3	1.05	24.20
11/20/16	2.95	27.15		
	3.0	27.15		
		27.1	2.95	24.16
11/20/16	2.7	26.9		
	2.7	26.9		
		26.85	2.65	24.20
				———
		Average Deflection		24.18 mm
		Scale Corrected		24.26 mm

k = 0.005080

0.4938 M Mannite

Date	Zero	Reading	Zero	Reading	Deflection
12/1/16	290.05	320.1			
	290.0	320.1	289.95	320.1	
	290.05	320.05	289.95	320.15	30.15
12/2/16		320.7	290.45	320.6	
		320.7	290.5	320.75	
		320.7	290.5	320.75	30.22
12/2/16	290.8	321.0			
	290.8	321.0	290.8		
		321.0	290.85		30.19
12/2/16	290.4	320.55			
	290.4	320.55	290.4		
		320.5	290.4		30.13
12/3/16	290.0	320.35			
	290.05	320.3			
		320.3	290.0		30.31
			Average Deflection		30.20 mm

k = 0.005109

0.5958 M Mannite

Date	Zero	Reading	Zero	Deflection
12/16/16	291.9	328.5		
	291.9	328.5	291.9	
		328.6	291.9	36.63
12/16/16	291.95	328.65		
	291.9	328.7		
		328.6	292.0	
		328.6	292.0	36.66
12/17/16	292.0	328.75		
	292.0	328.8	292.0	
	292.0	328.75	292.0	36.77
12/18/16	292.85	329.55		
	292.85	329.45		
		329.55	292.9	
		329.6	292.85	36.68
12/18/16	292.85	329.45		
	292.9	329.35		
		329.3		
		329.35	292.85	36.49
12/19/16	292.25	328.75		
	292.2	328.8	292.25	
	292.2	328.8	292.25	36.55
12/19/16	292.45	329.15		
	292.5	329.2	292.5	
		329.15	292.5	36.70
12/19/16	291.95	328.5		
	291.9	328.55		
		328.5	292.0	
		328.6	291.9	36.60
			Average Deflection	36.63 mm

k = 0.005109.

0.5944 M Mannite

Date	Zero	Reading	Zero	Deflection
12/10/16	289.2	325.9		
	289.2	325.8		
		325.8	289.3	
		325.7	289.3	
		325.8	289.3	36.54
12/10/16	289.3	325.85		
	289.3	325.8	289.35	
	289.3	325.9	289.3	36.54
12/10/16	289.5	326.0		
	289.4	326.0		
		326.05	289.4	36.59
12/11/16	295.2	331.85		
	295.1	331.8		
	295.2	331.75	295.2	
		331.75	295.25	36.60
12/11/16	295.7	332.35		
	295.7	332.25		
	295.75	332.35		
		332.15	295.75	36.55
12/11/16	295.0	331.6		
	295.0	331.5		
		331.55	295.0	36.55
			Average Deflection	36.56 mm

k = 0.005109

0.6934 M Mannite

Reading	Zero	Reading	Zero	Deflection
12/1/16	290.05	332.55		
	290.0	332.5	289.95	
	290.05	332.45	289.95	42.50
12/1/16		332.1		
		332.15		
		332.1	289.7	
		332.2	289.65	
		332.1	289.6	42.48
12/2/16		333.35	290.8	
		333.3	290.8	
		333.3		42.51
12/2/16	290.4	332.9		
	290.4	332.8	290.3	
		332.9	290.35	42.51
12/3/16	290.0	332.5		
	290.0	332.6	289.95	
	290.05	332.5	290.05	42.52
			Average Deflection	42.50 mm

k = 0.005109

0.7927 M Mannite

Date	Zero	Reading	Zero	Reading	Deflection
12/16/16	293.1	341.75			
	293.2	341.8	293.1		
	293.2	341.8	293.2		48.62
12/16/16	293.4	342.0			
	293.4	342.0			
	293.35	342.05	293.5		48.61
12/16/16	292.0	340.9			
	292.0	340.8			
	292.0	340,8	292.05		
		340.85	292.0		48.83
12/17/16		340.9	292.15	340.9	
		340.95	292.1	340.95	
		341.0	292.1	340.95	48.82
12/17/16	292.8	341.6			
	292.75	341.5			
	292.8	341.6			
		341.7	292.85		
		341.6	292.85		48.79
12/18/16	292.9	341.6			
	292.95	341.5			
		341.45	293.0		
		341.5	292.95		48.56
12/18/16	292.8	341.4			
	292.8	341.55	292.7		
		341.65	292.75		
		341.55	292.8		
		341.55	292.7		48.78
12/19/16	292.25	341.0			
	292.25	341.0			
		341.0	292.25		48.75
12/19/16	292.45	341.1			
	292.5	341.15			
		341.15	292.45		48.66

Average Deflection 48.71 mm

k = 0.005109.

0.8913 M Mannite

Date	Zero	Reading	Zero	Deflection
12/9/16	289.95	344.9		
	289.9	344.85		
		344.85	289.95	54.94
12/10/16	289.4	344.35		
	289.45	344.25	289.5	
		344.3	289.4	54.86
12/11/16	295.2	349.95		
	295.25	350.05		
		350.0	295.2	54.78
12/11/16	295.7	350.5		
	295.7	350.6		
	295.75	350.65		
		350.55	295.75	54.85
12/11/16	295.0	349.9		
	295.0	349.8		
		349.9		
		349.9	295.0	54.88
			Average Deflection	54.86 mm

k = 0.005109.

0.8922 M Mannite

Date	Zero	Reading	Zero	Reading	Deflection
10/11/16	7.0	62.1			
	7.0	62.0			
	7.0	62.1			55.03
10/13/16	3.9	59.0			
	3.9	59.0			
	4.0	59.0			
		58.95	3.95		55.05
10/14/16	2.2	57.2			
	2.1	57.1			
	2.2	57.2			55.00
10/16/16	2.0	57.0			
	2.0	57.05	1.9		
		57.0	1.9		55.07
10/18/16	2.9	57.95			
	2.9	57.95	3.0		
		57.85	3.0		54.97
10/19/16	2.0	57.1			
	2.0	57.05			
		57.05	2.0		55.07
				General Average	55.03 mm
				Scale Corrected	55.20

k = 0.005080

0.9908 M Mannite

Date	Zero	Reading	Zero	Deflection
11/17/16	2.95	63.9		
	2.95	63.9		
		63.85	2.9	60.95
11/18/16	2.1	63.05		
	2.1	63.05		
		63.05	2.1	60.95
11/19/16	1.15	62.1		
	1.05	62.05	1.05	
	1.1	62.05	1.05	60.99
11/20/16	2.95	64.0	2.9	
		64.0	3.0	
		64.0	3.0	61.04
11/20/16	2.65	63.7		
		63.7	2.7	
		63.6	2.65	60.99

Average Deflection 60.98 mm

Scale Corrected 61.20 mm

k = 0.005080

Table 2 -- SUMMARY OF DATA.

G = grams of Mannite per 1000 grams of Water (in vacuo)
$p_o - p_1$ = vapor pressure lowering in mm Mercury (Mercury corrected to 0°)
Calc = Lowerings calculated according to Raoult's law
Diff = Difference between Calculated and Observed Lowerings

G	M	s	$k \times 10^{-6}$	h(24)	$p_o - p_1$	Calc	Diff	Mol Fract $\times 10^{-4}$	$\frac{p_o - p_1}{n/N+n}$	$\frac{p_o - p_1}{M}$
17.930	0.0984	6.06	5080	0.0308	0.0307	0.0311	0.0004	17.70	17.31	0.3113
36.004	0.1977	12.15	5080	0.0617	0.0614	0.0622	0.0008	35.48	17.32	0.3108
53.951	0.2962	18.23	5080	0.0926	0.0922	0.0931	0.0009	53.09	17.37	0.3113
71.917	0.3945	24.26	5080	0.1232	0.1227	0.1239	0.0012	70.64	17.37	0.3107
89.938	0.4938	30.20	5109	0.1542	0.1536	0.1547	-0.0011	88.18	17.42	0.3111
108.243	0.5944	36.56	5109	0.1871	0.1860	0.1858	-0.0002	105.94	17.55	0.3129
108.498	0.5958	36.63	5109	0.1868	0.1863	0.1862	-0.0001	106.18	17.55	0.3128
126.283	0.6934	42.50	5109	0.2171	0.2162	0.2164	0.0002	123.38	17.62	0.3118
144.357	0.7927	48.71	5109	0.2489	0.2478	0.2469	-0.0009	140.79	17.60	0.3126
162.332	0.8913	54.86	5109	0.2803	0.2791	0.2772	-0.0019	158.03	17.66	0.3131
162.485	0.8922	55.20	5080	0.2804	0.2792	0.2775	-0.0017	158.19	17.65	0.3129
180.451	0.9908	61.20	5080	0.3109	0.3096	0.3076	-0.0020	175.37	17.65	0.3124

DISCUSSION OF RESULTS.

Accuracy of the Method. The chance errors of observation are very small as will be seen by a consideration of probabilities. It will be observed that always as many as three values were taken on the zero point and on the deflection reading. The average error of the zero point setting was about 0.03 mm scale deflection. Putting the average error of the deflection reading at 0.04 mm this gives an average error of each measurement of $\sqrt{0.03^2 + 0.04^2} = 0.05$ mm. If five observations are taken the average error of the final value for the deflection is 0.01 mm scale deflection. The probability that a given series of observations will be within this range is about four-sevenths. In other words, under the conditions of the work the error of the observation of the lowering will be within 0.01 mm scale deflection four times out of seven. This is but 0.00005 mm actual lowering. However, this does not represent at all the accuracy of the method, for there are certain constant errors whose relative values are additive in calculating the final error: 1. There is a slight amount of air present. 2. The solutions concentrate somewhat by evaporation before an analysis can be made. 3. There is a possibility that the surface concentration of the solution is not entirely overcome by stirring the solution during the reading. Altogether it is evident that the method is limited

in its accuracy by these factors and not by errors of observation; 1. Measuring the deflection. 2. Determining the constant k. 3. Analyzing the solution.

Raoult's Law. Table 2 shows a summary of the results and gives the deviation from Raoult's law. In calculating theoretical lowering the equation

$$\frac{p_o - p_1}{p_o} = \frac{n}{N + n}$$

was used, where, p_o = the vapor pressure of the pure solvent at the same temperature. This has been accurately determined by Holborn and Henning and by Scheel and Heuse who give identical values — 17.539 mm. p_1 = the vapor pressure of the solution. n = the number of mols of solute, and N = the number mols of solvent. The agreement with experimental values of lowerings thus calculated is much closer than when the old form of Raoult's law is used,

$$\frac{p_o - p_1}{p_o} = \frac{n}{N}.$$

It will be seen that the observed values are increasingly lower than the calculated until a minimum deviation is reached at about 0.4 M. At about 0.6 M the calculated and observed are the same, and it is not until a higher concentration is reached that there is a marked deviation from Raoult's law. However, although the deviation in the range 0.1 to 0.8 M is never much greater than the 0.001 mm claimed as the accuracy of the

method, it must be emphasized that the results are relatively accurate enough to allow us to draw some conclusions from these deviations. In support of this statement the close agreement of the two lowerings at 0.6 M and 0.9 M, where the actual discrepancy is less than 0.0002 mm, is a strong evidence of the relative accuracy. Therefore we may recognize the fact that mannite solutions behave regularly up to 0.5 M concentration. But beyond that point irregularities begin to occur. The significance in the minimum molecular lowering at 0.4 M is probably explained by the anomalies of the solvent, for such minima frequently occur at this concentration in the colligative properties of aqueous solutions. An explanation will probably be found in the complex character of water.

It is often the custom to examine vapor pressure results in the light of the molecular lowering value, $p_o - p_1 / M$, and for that reason this value has been plotted against concentration in figure 4. However, this function has no theoretical significance as will be seen; since

$$p_o - p_1 = p_o \frac{n}{N + n}$$

the molecular lowering

$$\frac{p_o - p_1}{n} = \frac{p_o}{N + n} .$$

The function, $p_o / N + n$, is a decreasing one, as a function of n. It seems that it is often thought that molecular lowering should be constant, but for an ideal solution the molecular lowering curve is concave downward, only slightly

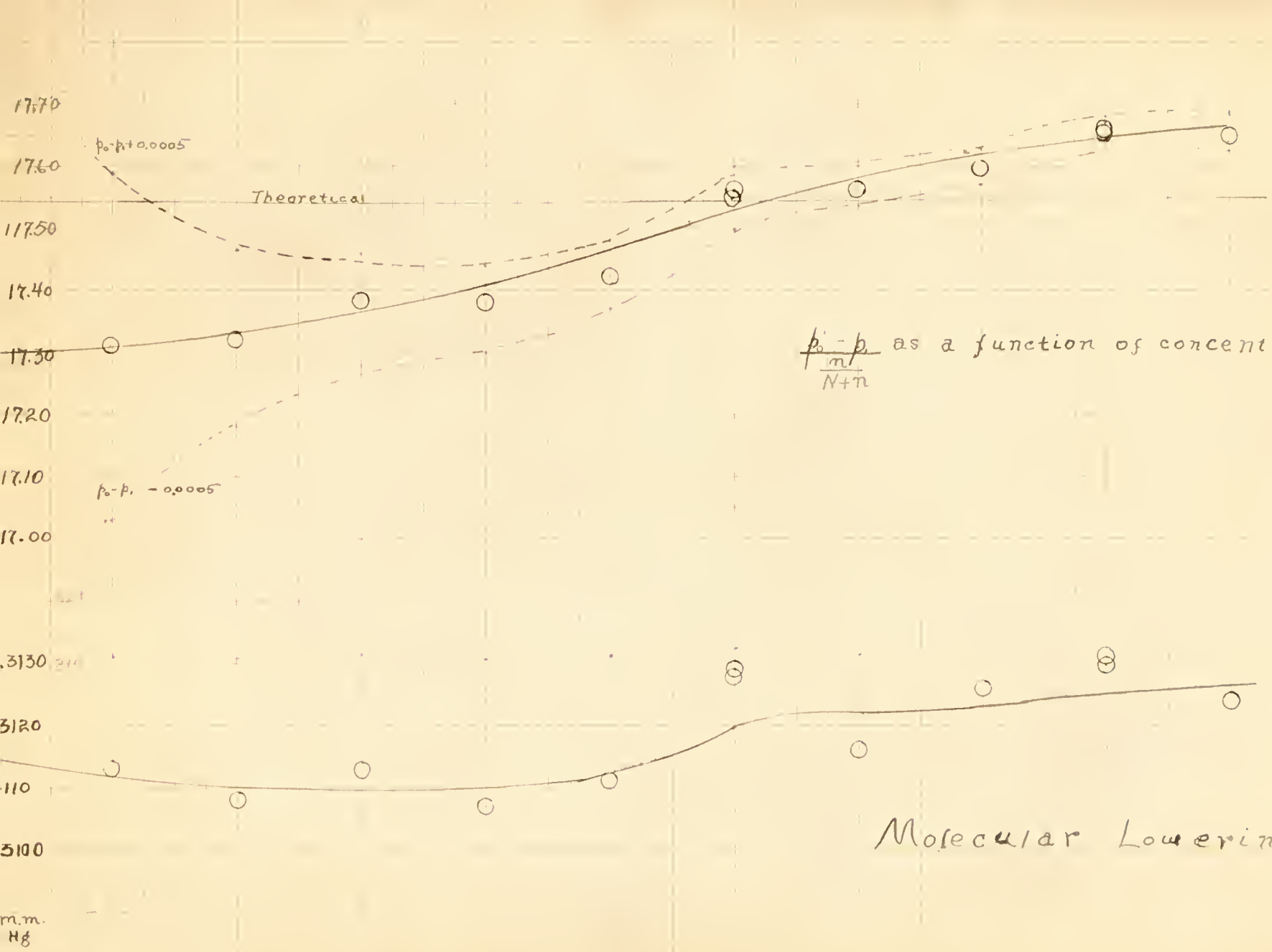
17.70
17.60
17.50
17.40
17.30
17.20
17.10
17.00
$p_o - p + 0.0005$
Theoretical
$p_o - p_1 - 0.0005$
$\frac{p_o - p}{\frac{m}{N+n}}$ as a function of concentration.
.3130
3120
110
3100
m.m. Hg
Molecular Lowering

Fig 4

however in dilute solutions. Thus it is evident that conclusions drawn from the molecular lowering curve may be misleading.

Therefore it seems logical to calculate the value of the lowering divided by the mol fraction, which according to Raoult's law is a constant, viz., the vapor pressure of water at the temperature in question.

$$\frac{p_o - p_1}{\frac{n}{N + n}} = p_o.$$

This function has a real meaning, then; it is the lowering which an involatile solute would give if its concentration were infinite, an infinitesimal amount of the solvent being present. There would obviously be no vapor pressure. The lowering would be exactly equal to the vapor pressure of the pure solvent. The value of this function is plotted against concentration in figure 4. The dotted lines represent what the value would be if there were a deviation of plus or minus 0.0005 mm from the lowering found. An examination of the curve gives one a clear and accurate idea of the bahavior of mannite solutions. The rise in the curve in the higher concentrations is probably attributable to increasing hydration. It is unfortunate that we are limited in further investigation by the solubility of this substance.

Von Babo's Law and the Heat of Dilution. The temperature coefficient of the vapor pressure of solutions is of interest, and for this purpose comparison of the results at 20 degrees with those at other temperatures will be made. There is not any data of sufficient accuracy on the vapor pressure of mannite solutions at other temperatures and we resort to indirect comparison by means of boiling point and freezing point data.

The relation between the freezing point lowering and the vapor pressure is an application of the Clausius-Clapeyron equation --

$$\frac{d \ln p}{dt} = \frac{L_F}{RT^2} ,$$

which represents the vapor pressure of ice as a function of the temperature, and the vapor pressure of the solution is the same as that of ice at that temperature. By integrating the equation and evaluating the constant, one obtains the expression,

$$\ln \frac{p_o}{p_1} = \frac{L_F \Delta t}{R T_o T_F} ,$$

which is the relation desired. L_F is the molal latent heat of fusion of ice, assumed to be constant over the range of temperature, Δt, which is the freezing point lowering of the solution. T_o is the freezing point of the pure solvent, and T_F that of the solution.

Vapor pressure values may be obtained from boiling point elevation values by application of the same fundamental equation, but a surer method is to find the atmospheric pressure from the boiling temperature of the pure solvent. This becomes p_1, the vapor pressure of the solution, when the boiling temperature is raised slightly above that of the solvent. Then the vapor pressure of the pure solvent for that final temperature is found by the use of tables. This gives p_o and p_1 at the same temperature.

Von Babo's law states that the relative lowering of vapor pressure is independent of the temperature. And Kirchhoff's equation for the heat of dilution is a quantitative statement of the deviations from von Babo's law.

$$H = R\,T^2 \frac{\partial}{\partial t} \left(\ln \frac{p_o}{p_1}\right)$$

H is the heat of dilution and is defined as the heat which must be added to keep the temperature constant when one gram of solvent is added to an infinite amount of solution. Von Babo's law may be said to be a special case of Kirchhoff's equation and merely states that

$$\frac{\partial}{\partial t}\left(\ln \frac{p_o}{p_1}\right) = 0$$

Hence the function $\ln p_o/p_1$ is a very convenient one to use in dealing with the variation of vapor pressure with temperature.

Juttner has calculated the value of this function for the value of this function. For mannite solutions[1] the freezing point data was that of Loomis,[2] and the ebullioscopic measurements were Beckmann's.[3] In table 3 will be found these values of ln p_o/p_1 as given by Juttner and in addition the values at 20 degrees from this vapor pressure work are given. The concentrations have been extrapolated slightly in order that direct comparison may be made. In figure 5 these values for the three temperatures are plotted against concentration. The boiling point values lack smoothness, the lowest concentration 0.131 M seems to be quite out of line, but the general trend of the curve can be seen clearly. No very refined work has been done on the freezing point lowering of mannite solutions at ordinary concentrations. Adams[4] working in dilute solutions has shown Loomis to be a little in error, but this is negligible for the present comparison. The most concentrated solution measured by Hall and Harkins,[5] using Adams' method, was 0.1197 M, and gives a value of ln p_o/p_1 of 0.00217 as against 0.00213 for the vapor pressure value for the same concentration. This compares very favorably with the agreement between Loomis' and the vapor pressure value.

1. Z. physik. Ch., 38, 110 (1901)
2. ibid 32, 599
3. ibid 6, 459 (1890)
4. J. Am. Chem. Soc., 37, 481 (1915)
5. ibid 38, 2658 (1916).

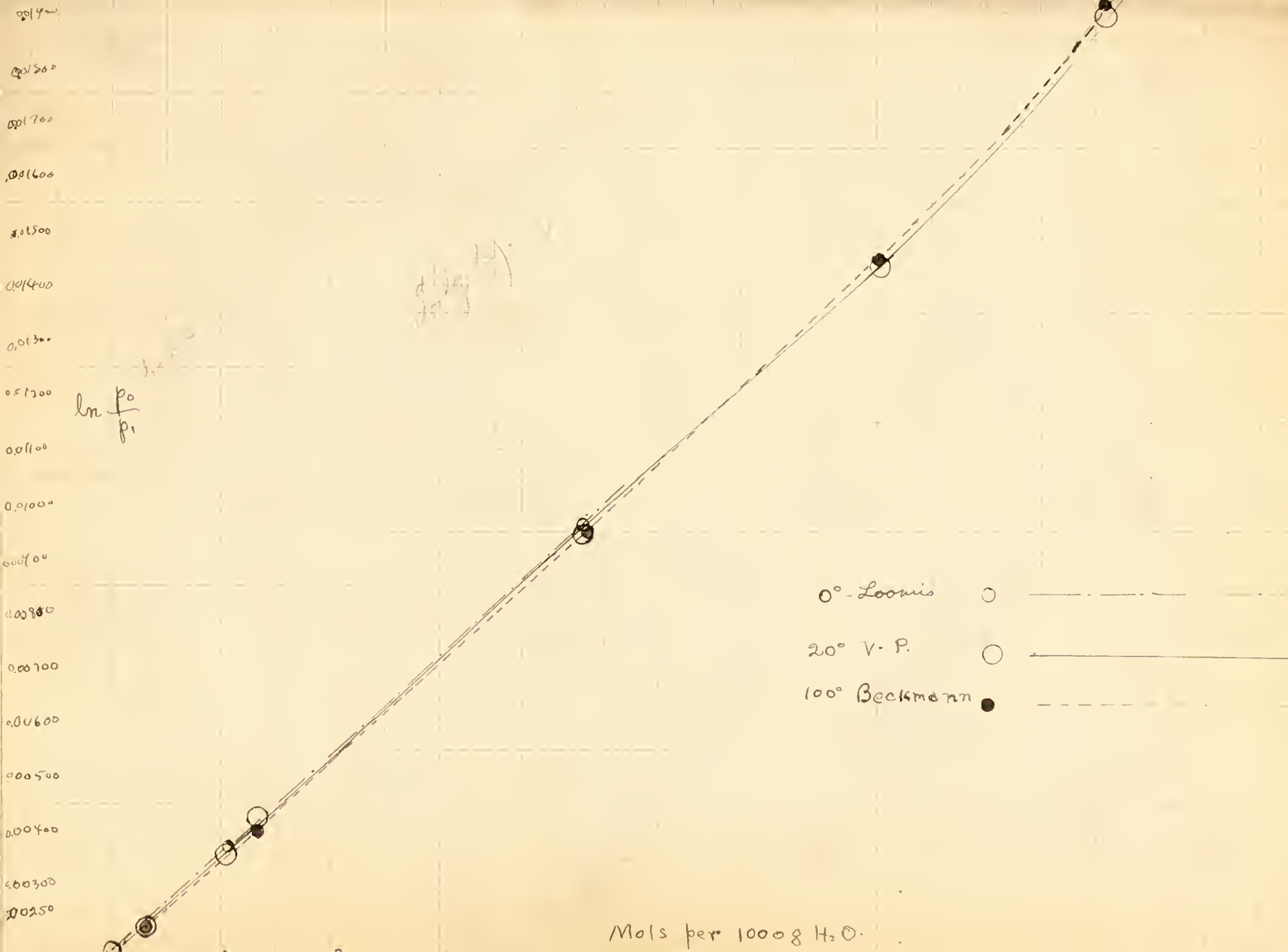
$\ln \frac{p_0}{p_1}$
0° - Loomis
20° V. P.
100° Beckmann
Mols per 1000 g H_2O.

Table 3 — Comparison of Vapor Pressure Ratios with Calculated Values.

M	$p_o - p_1$ 20^o	ln p_o/p_1		
		0^o	20^o	100^o
0.1013	0.0315	0.00184	0.00180	
0.131	0.0408		0.00233	0.00235
0.2061	0.0641	0.00373	0.00358	
0.268	0.0834		0.00479	0.00451
0.5323	0.1656	0.00964	0.00945	
0.537	0.1671		0.00957	0.00951
0.801	0.2504		0.01438	0.01448
1.058	0.3305		0.01902	0.01915

An examination of the table and curves shows that the ln p_o/p_1 curve at 100 degrees lies slightly under that for zero degrees. The twenty degree values, with the greater range of concentration, prove more interesting. It can be seen that in dilute solution the deviations are comparatively slight and increase with concentration for a time, but in the concentrated solutions the value of ln p_o/p_1 at 100 degrees lies above that for twenty. This phenomenon of the change of the sign of the heat of dilution with increasing concentration is often evidenced in aqueous solutions. It is needless to say that von Babo's law does not hold in the concentrations studied. Further, the data seems to indicate that the heat of dilution is numerically greater at lower temperatures than

at higher, since $\frac{\partial}{\partial t}(\ln p_o/p_1)$ is greater between zero and 20 degrees than between 20 and 100 degrees. Finally it may be said that the results indicate that the heat of dilution (as defined above) of mannite solutions changes from negative in dilute to positive in concentrated solutions, and that further experimental evidence at different temperatures is very desirable.

OSMOTIC PRESSURE OF MANNITE SOLUTIONS

From what has been said regarding the heat of dilution of mannite solutions it follows that for quantitative correlation, other colligative properties must be investigated at the same temperature. For this reason it was decided to study the osmotic pressure of mannite solutions over the same range of concentration at 20 degrees.

Experimental. The methods and apparatus used were those as developed by Morse and Frazer[1] and modified by Frazer and Myrick.[2] The experimental details were carried out in practically the same manner as in the previous osmotic investigations. For measuring the pressures glass manometers were used rather than the resistance gauge, which is applicable for higher pressures.

An important feature introduced was the careful analysis of the solutions after the cell was taken down. The interferometer here was used as described above. The osmotic pressures of mannite solutions from 0.1 to 0.5 M had been measured,[3] but since the solutions were not analyzed after the experiment the results were not recorded as final. The solutions and solvent were made up to be isotonic with very dilute copper sulphate and potassium ferrocyanide, except in one case, where equilibrium was apparently never established.

1. Carnegie Publication: Osmotic Pressure of Aqueous Solutions

2. J. Am. Chem. Soc., 38, 1907. (1916)

3. Dissertation J.H.U., E. L. Frederick (1914)

All the manometers utilized except one had been under high pressures from previous experiments. The volumes were therefore redetermined. The value for manometer No. 37 was found to be very near the original volume, and the old value was used. It is practically certain that any flow of the glass which takes place is in the wide portion of the manometer, below the calibrated capillary. When measurements are being taken all readings concerned are on the thick bore capillary and it seems perfectly safe to assume that its original calibration is correct. Manometer No 34 did not seem to give values in accord with the others and by comparison with a reliable manometer was found to be considerably off. The volume was determined again and a 1% correction was applied.

The cells were kept up until the pressure recorded was the same for two days or more. Follows a table showing the osmotic pressures of solutions approximately 0.2, 0.4, 0.6, 0.8, and 1.0 molar. Attempt was made to get two measurements on each concentration.

Table 4 -- Osmotic Pressure Data.

G	M	Manom No.	P	P/M	
35.88	0.1970	62	4.84	24.57	
*36.08	0.1981	62	4.73	23.88	No equilibrium
70.87	0.3891	37	9.27	24.38	
71.25	0.3912	34	9.50	24.28	
*106.60	0.5853	35	13.84	23.64	Manometer doubtful
107.81	0.5920	37	14.31	24.17	
141.72	0.7782	34	18.95	24.35	
142.97	0.7850	37	19.03	24.24	
178.50	0.9801	37	23.50	23.98	
179.20	0.9840	34	24.20	24.57	

Osmotic Pressure and Vapor Pressure. Porter[1] has developed a general equation connecting the osmotic pressure and vapor pressure of solutions of any degree of compressibility.

$$\int_{p'}^{P_h} V_s \, dP = \int_{p_1}^{p_o} v \, dp + \int_{p_o}^{P_h - P_p} V \, dP$$

To use this equation for small pressures we may omit the compressibility work term, $\int_{p_o}^{P_h - P_p} V \, dP$. Integrating by use of the gas law, the simplified equation

$$P \, V_S = R \, T \ln \frac{p_o}{p_1}$$

is obtained. V_S is the increase in volume when one gram of solvent is added to a large amount of solution. Gouy and

1. Proc. Roy. Soc., 79 A 519 (1907)

Chaperon[1] give the expression

$$V_s = \frac{1}{d}\left(1 + \frac{s}{d}\frac{dd}{ds}\right)$$

in which s is the percentage solute and d the density. Densities of a number of mannite solutions at 20 degrees were determined with a modified Sprengel pycnometer.

This gives all the data necessary to calculate the osmotic pressure of a solution whose vapor pressure is known. The densities increase regularly with the concentration, and the values were extrapolated only slightly from the original data. Table 5 gives the results of these calculations. The best values observed directly corresponding to the concentrations named are given in the last column.

Table 5--Calculated Osmotic Pressure.

M	d	V_s	P Calc	P obs.
0.0984	1.0044	1.0021	2.327	
0.1977	1.0104	1.0021	4.680	4.86
0.2962	1.0163	1.0016	7.023	
0.3949	1.0221	1.0015	9.391	9.59
0.4938	1.0277	1.0016	11.73	
0.5958	1.0333	1.0020	14.24	14.40
0.6934	1.0385	1.0018	16.53	
0.7926	1.0439	1.0015	18.97	19.21
0.8913	1.0489	1.0015	21.39	
0.9908	1.0538	1.0013	23.75	24.12

1. Ann. Chim. Phys. (6) 12, 387 (1887)

It can be seen that the values calculated from vapor pressure are approximately the same amount lower than the observed over the entire range of concentration. This is somewhat unexpected as the behavior of water under pressure would lead one to think that the concentration of solutions is decreased under pressure due to a change of mol fraction of the solvent. The only assumption made in the calculations is that the vapor pressure of water obeys the gas law over a slight range. It is generally accepted that this is permissible, although little accurate data supports the assumption. The range of pressure is so slight that it would seem that no appreciable error is introduced, since Batelli gives a variation in pv for water vapor at 21° of only 0.1 % over a range of 10 millimeters pressure.

However, the experimental data cannot be considered to be in final form since there is considerable uncertainty as to the absolute accuracy of the manometers used. Until measurements which cannot be questioned are obtained, it is not profitable to draw conclusions as to the agreement cited in Table 5.

SUMMARY

The vapor pressure lowerings of aqueous solutions of mannite have been investigated at 20 degrees over the entire range of solubility.

An improvement in the method for preparing and introducing solutions has been accomplished, effecting a more complete removal of air in a much shorter time.

The results are discussed from the standpoint of Raoult's law and comparison is made with freezing point and boiling point data.

The osmotic pressure of mannite solutions has been measured and compared with the values calculated from the vapor pressures observed.

BIOGRAPHY

The author of this dissertation was born in Kentucky January 25, 1895. He received his early education in the public schools of Lexington, Ky. He was graduated from Centre College, Danville, Ky., in 1914, receiving the degree of Bachelor of Arts. In the fall of 1914 he entered the Johns Hopkins University as a graduate student in Chemistry. Physical Chemistry and Mathematics were his subordinate subjects. During the years 1915-16 and 1916-17, he was appointed Hopkins Scholar.